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ORIGINAL ARTICLE

PdNi-coated manganite nanorods as catalyst for electrooxidation of methanol in alkaline medium

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Abstract Palladium and Nickel (PdNi) were coated on the manganite nanorods (MN) by a in situ reduction method. The prepared nanocatalyst was characterized by powder X-ray diffractrogram (XRD), scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDS) and electrochemical studies. The XRD patterns and EDS measurements confirm the formation of nanocrystalline PdNi on the surface of the MN. This nanocatalyst was tested for the electrooxidation of methanol in alkaline medium. The PdNi/MN catalyst modified electrode shows improved current response when compared with Pd/MN and Pd/C modified electrodes. The forward oxidation potential was shifted negative and the backward oxidation current was minimized compared with Pd/C. The electrooxidation of methanol was studied at various concentrations of KOH and methanol. The methanol electrooxidation exhibits highest current response for 9 M KOH/6 M CH_3OH solution. The presence of MN act as excellent support material and help in the electrocatalytic activity of PdNi.

Keywords Methanol electrooxidation · Manganese oxide · Palladium · Nickel · Fuel cell

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Introduction

Recently, alternative sources of energy have been of intensive concern due to environmental problems and also because of the decline in the availability of fossil fuels. The direct methanol fuel cell (DMFC), as one of the potential power sources for portable electronic devices or transportation vehicles, has increasingly attracted a great deal of attention due higher energy efficiency, low emission. DMFCs are promising electrochemical power sources for mobile, stationary and portable applications, and the electrocatalytic oxidation of methanol has been studied extensively. (Bianchini and Shen 2009; Suresh kumar et al. 2008; Leger 2001).

In the field of fuel cell research much attention has been paid for the preparation of metal catalyst in the nanoscale. Up to date, most of the researches on DMFC have been done using Pt and Pt-based alloys as anode catalysts due to their high catalytic ability. However due to the limited resources of Pt, higher adsorption of CO as poising agent, noneffective methanol cross over etc., nonPt-based catalysts such as Pd-based catalyst has been widely studied for the methanol oxidation reaction (MOR) (Singh et al. 2009; Qi et al. 2011; Goodenough et al. 1987, 1988; Trasatti 1981; Shibata and Motoo 1986; Xu et al. 2008). Palladium (Pd), a Pt group elements available in abundance and is of low cost when compared to Pt, which makes it attractive for usage as electrochemical anode catalyst for DAFCs (Trasatti 1981; Shibata and Motoo 1986; Xu et al. 2008; Liu et al. 2009; Maiyalagan and Scott 2010).

The poisoning of the active site of catalyst is the major drawback in DAFC. In order to reduce this poisonous effect various methods were adopted, such as placing a metal adjacent to the catalytic metal (Goodenough et al. 1987, 1988), alloys (Qi et al. 2011) or placing the catalyst

on a suitable support (Maiyalagan and Scott 2010; Miao et al. 2010; Zhao et al. 2010). By imparting metals such as ruthenium, gold, palladium, bismuth, lead to Pt/Pd, the poisoning of catalyst surface as well as the cost of the catalyst can be minimized (Goodenough et al. 1987, 1988; Trasatti 1981; Shibata and Motoo 1986). Similarly, Ni has also been used. The introduction of Ni to Pd, an oxophilic element enhances the adsorption of OH^- resulting in the oxidation of the chemisorbed intermediates effectively. Investigations in this direction have just begun. Recently, various supporting materials including carbon nanotubes (Maiyalagan and Scott 2010), carbon nanofibers (Miao et al. 2010), metal oxides (Zhao et al. 2010; Wei et al. 2011; Vracar et al. 1998) etc., have been used as supporting material for various DAFCs. Among these, metal oxides exhibits improve catalytic activity, because they readily donate oxygen atom to the catalyst, improving the catalytic activity (Zhao et al. 2010).

Transition metal oxides as supporting materials for Pd have also been used as catalysts for alcohol oxidation which significantly improves the electrode performance by enhancing the electrochemical activity (Xu et al. 2008; Liu et al. 2009). Recently, PdNi bimetal on various support material such as carbon (PdNi/C) (Maiyalagan and Scott 2010; Miao et al. 2010), Si nanowires (Zhao et al. 2010), alumina (Qi et al. 2011) CeO_2 (Vracar et al. 1998) and MWCNT (Singh et al. 2009; Wei et al. 2011) for alcohol electrooxidation in alkaline media was investigated. In this work, small quantities of Pd (5 and 10 wt%) was tested in the presence of Ni coated on MN which were synthesized by in situ reduction method. The prepared nanocatalyst was tested for the electrooxidation of methanol in alkaline medium. The nanocatalyst exhibits an enhanced electrocatalytic activity with higher stability.

Experimental

Palladium chloride (Sigma-Aldrich), Nickel acetate, Potassium permanganate, Hydrogen peroxide (30% W/W), acetic acid, sodium acetate, Potassium hydroxide, and Methanol received from Merck, India. All the chemicals were of analytical grade and were used without further purification.

The MN was prepared as follows, about 100 ml of a aqueous $KMnO_4$ (0.55 M) was subjected to soniciation. Hydrogen peroxide (10 ml) and Acetate buffer (5 ml) mixer was added drop wise into it and the sonication was continued. After 1 h the colloidal solution was subjected to refluxing at 60°C for 24 h. The resulting product was separated, washed and dried.

Suitable quantity of 0.5 mm $PdCl_2$ and $Ni(ac)_2$ solutions were taken in 5 ml of ethanol, so as to achieve 5:10 wt% or 10:10 wt% of Pd/Ni and 100 mg of MN was added and stirred. After 1 h formaldehyde was added to the mixture drop wise and a reductive reaction was performed at room temperature. After 6 h, the resulting product was filtered washed with distilled water, and then dried at 60°C for 6 h. The prepare MN and PdNi/MN was characterized by powder XRD (Schimadzu Lab X–6000), SEM (JEOL 6390). EDS (INSTA FET, Oxford instruments) and TEM (JEOL, JSM 2100).

The glassy carbon electrode (GC, 3 mm diameter) was first polished with Al_2O_3 slurry. PdNi/MN nanocomposite was ultrasonically dispersed in 0.05% of Nafion in ethanol solution. An aliquot of the PdNi/MN nanocomposite/Nafion suspension was dropped on the surface of the GC electrode and allowed to dry. Electrochemical measurements were performed with a CHI660C electrochemical workstation (CH Instruments, Austin, USA) and a conventional three electrodes cell equipped with computer controlled software. The PdNi/MN nanocatalyst modified GC electrode was the working electrode, a Pt wire served as the counter electrode and a standard calomel electrode (SCE) was the reference electrode. For comparison, Pd supported on graphite powder and their electrodes were also prepared under the same preparative conditions. All potentials have been measured and reported with respect to SCE in this report. All the measurements were performed at room temperature.

Results and discussion

Physical characterization of MN and MN/PdNi nanocomposite

The powder XRD patterns of the nanotubular MN and PdNi-coated MN is shown in Fig. 1. The XRD peaks at $2\theta = 26$ (111), 33.9 (020) can be assigned to MN and this matches well with the JCPDS # 41–1379. The smoothened profile of PdNi modified MN nanocomposite exhibits similar patterns of MN with peaks for PdNi (111) at $2\theta = 41.2°$ and a few peaks for NiO and Pd are also seen (Qi et al. 2011). The surface morphology of the MN and PdNi/MN was characterized by TEM (Fig. 1b, c). The TEM images show bundles of nanoclusters of MN and a isolated nanorod is shown in Fig. 2a, b. Figure 2c shows the presence of nanocrystalline PdNi on the walls (red colored circle) of MN (indicated by orange colored arrow) and the lower magnification exhibits the uniformly coated PdNi on the MN (Fig. 2d).

EDS analysis were carried out to get local information of chemical properties of catalyst. EDS analysis was carried out by microprobe analysis of various portions of the catalyst thin film. It was observed that the relative intensities of Pd and Ni on MN signals were almost same and no

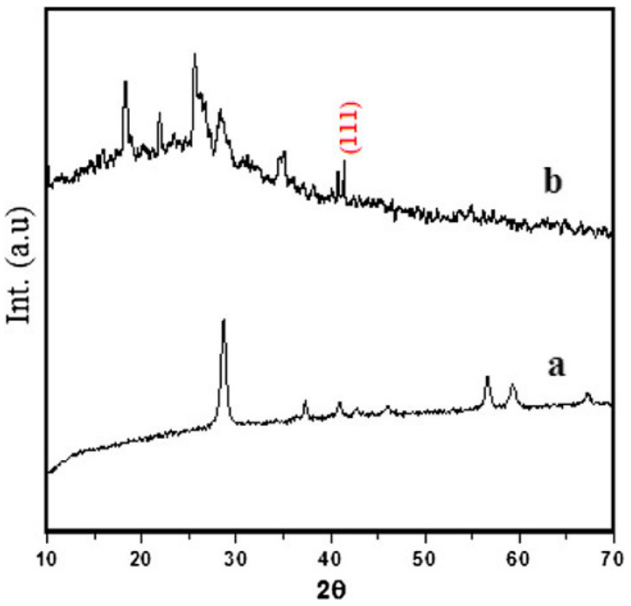

Fig. 1 X-ray diffractrogramme of the **a** Manganite nanorods and **b** PdNi-coated MN

significant changes were shown in Fig. 3. EDS spectrum of PdNi/MN catalyst, and atomic ration of composite is about 1:1.3 (Pd:Ni) on MN. The small oxygen peaks were observed, which means that some Ni atoms exist as NiO. This was supported by the XRD data.

Electrooxidation of methanol at MN/PdNi modified electrode

Figure 4A shows the cyclic voltammograms of Pd and PdNi on MN support in 1 M KOH solution. In the positive sweep, the PdNi and Pd on MN-modified GC electrode exhibit a peak at −0.81 (Fig. 2a, b) and −0.79 V (Fig. 4Aa), respectively, corresponding to the surface ad/absorbed hydrogen. The difference in the current response is due to adsorption of OH^- by the Ni in the catalyst. The peaks at E >−0.2 V correspond to the formation of mono Pd oxide layer. The mechanism of oxide formation is still unclear (Vracar et al. 1998), and it has been widely accepted that the OH^- ion is initially adsorbed on the Pd (Reaction 1), which

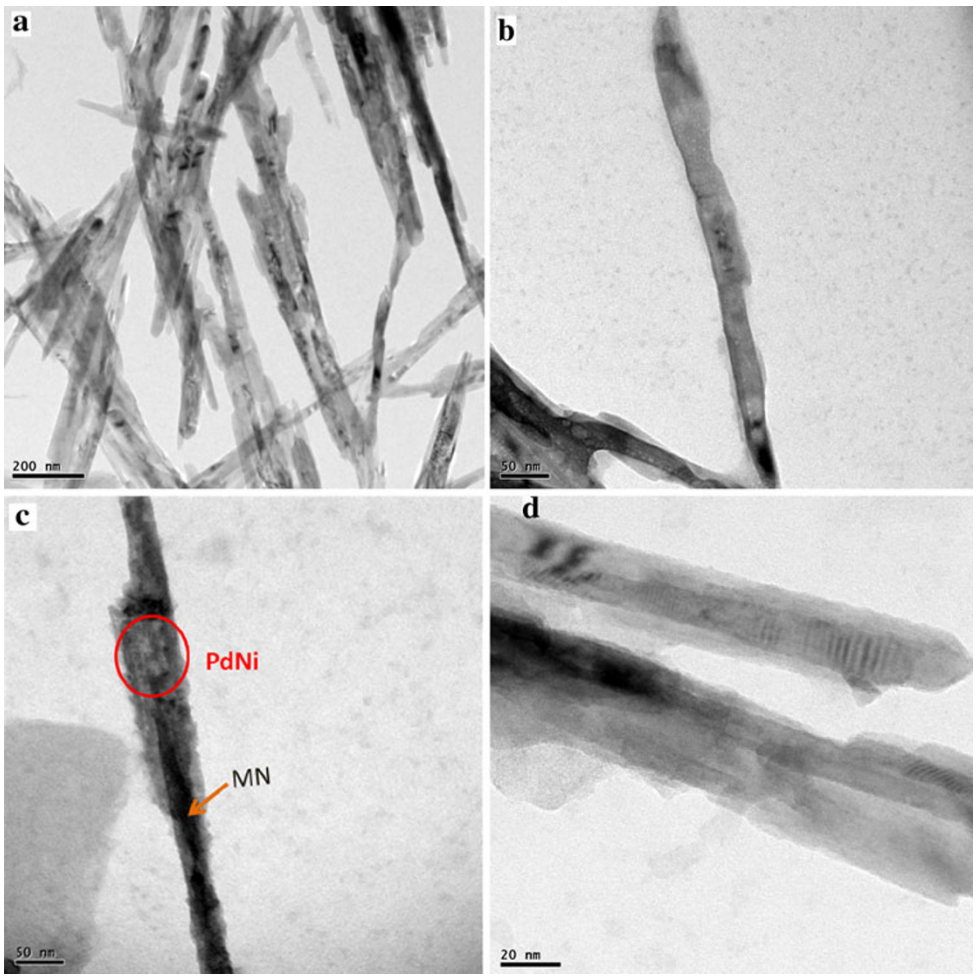

Fig. 2 Transmission Electron Microscopy of MN **a** nanoclusters, **b** nanorods and **c**, **d** nanocrystalline PdNi-coated MN

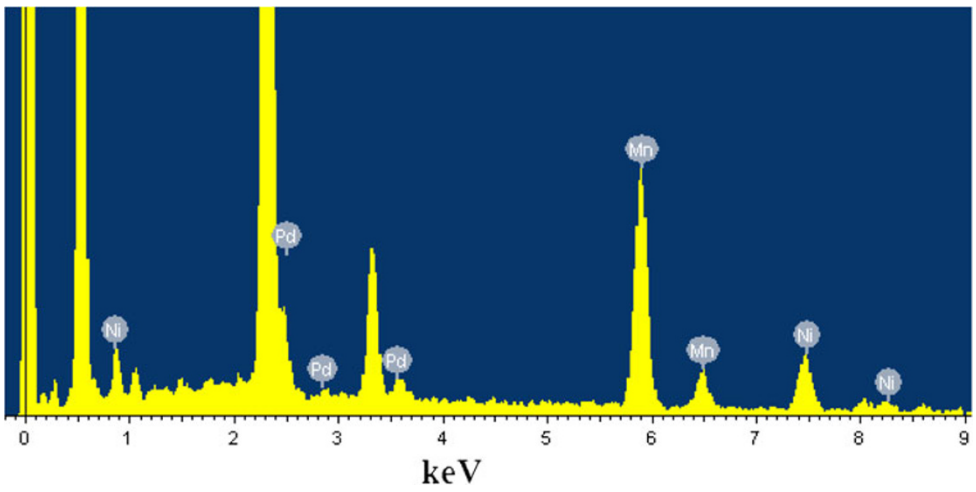

Fig. 3 Energy dispersive X-ray spectroscopy of nanocrystalline PdNi-coated MN

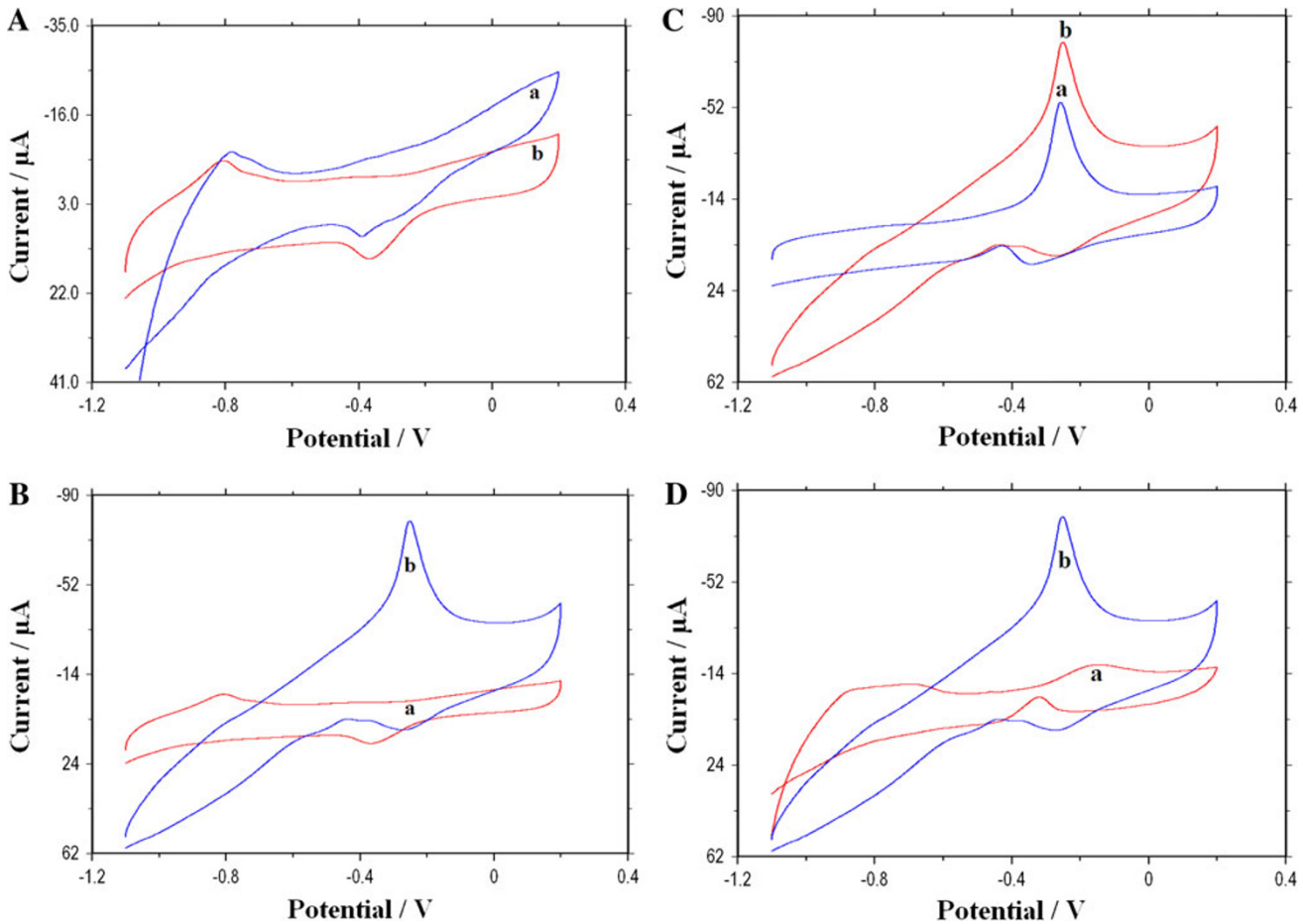

Fig. 4 Cyclic voltammogrames of GC modified **A** *a* Pd/MN *b* PdNi/MN in 1 M KOH; **B** PdNi in (*a*) 1 M KOH (*b*) 1 M KOH/1 M CH_3OH; **C** electrooxidation of Methanol *a* Pd and *b* PdNi/MN and **D** electrooxidation of Methanol (1 M KOH/1 M CH_3OH) in *a* Pd on fine graphite powder and *b* PdNi/MN

can be transformed to oxides at higher potential and further it helps to oxidize the methanol during the reaction. Further, at −0.365 V (PdNi) and −0.39 V (Pd) during the cathodic sweep the Pd (II) is reduced to Pd. This is due to active oxygen supplied by the supporting MN material which would facilitate the reduction. Figure 4Ba, b shows the cyclic voltammograms of the absence and the presence of methanol in the PdNi/MN catalyst modified electrode, which confirms the oxidation peak, to be due to the methanol oxidation by the catalyst.

The methanol oxidation reaction starts around −0.8 V and a vertex potential at −0.27 V is observed during the forward scan and second oxidation of surface chemisorbed intermediates at −0.418 V. The hydrogen adsorption region −0.81 V is significantly suppressed in the methanol electrooxidation in the alkaline solution, due to the dissociative adsorption of methanol molecules on the catalyst. The oxidation was clearly shown after −0.81 V, which may be attributed to the effective participation of OH^- ion. It is generally believed that these Ni species are oxophilic like Ru, and have the capacity to generate OH_{ads} at a lower potential, to facilitate the oxidation of the intermediate products, thus enhancing the catalytic activity of Pd catalyst (Bambagioni et al. 2009; Manoharan and Prabhuram 2001).

The cyclic voltammograms of Pd/MN and PdNi/MN (5% of Pd; Fig. 4Ca, b) in 1 M KOH/1 M CH_3OH solution has been compared, and it indicates that the PdNi/MN exhibits a higher electrocatalytic activity with enhanced current response compared to Pd/MN. The vertex potential is almost the same for both Pd as well as PdNi-coated MN systems (Fig. 4Ca, b). The PdNi/MN with Pd/C was studied for the electrocatalytic behavior in MOR. The vertex potential Ep = −0.27 V for PdNi/MN is negatively shifted by ∼150 mV compared to Pd/C (Fig. 4Da, b). This clearly indicates that the presence of Ni does not alter the peak potential, however MN readily supply active oxygen to the catalyst, which subsequently oxidize the ad/absorbed poisonous intermediates and extract OH^- from the solution and reconstruct the surface. Hence, the vertex oxidation potential is shifted to a lower region compared to that of Pd/C. Another interesting characteristic result that was observed is that the 11th cycle exhibits a higher current response compared to the first cycle, and one can infer that the PdNi/MN by this method towards MOR is closely related to the potential cycling number, and it seems that more potential sweeping cycles favor the process of MOR.

Figure 5A, B shows the cyclic voltammograms of MOR on the PdNi/MN on GC electrode in 1 M methanol solution containing various concentration of KOH ranging from 1–9 M. The peak potential was continuously shifted negative with increased peak current response which was observed with an increase in KOH concentration. At high pH, methanol oxidation rate increases appreciably, which is due to the change of the reactant from CH_3OH to CH_3O^- and of adsorbed intermediate from ≡C−OH to ≡C−O^-. The states of oxidation of the Pd surface also change at alkaline pH and the anionic adsorption is diminished. In all these concentrations the featured peaks were observed both as forward and backward oxidation peaks, which indicate that the prepared nanocomposite-coated GC electrode was smooth like the noble metals (Manoharan and Prabhuram 2001). Figure 5B shows the peak current was increased with increasing concentration up to 9 M KOH. The highest current was observed at 6 M KOH/9 M CH_3OH (Fig. 5Bb). The observed backward oxidation peak current density was very less due to the presence of manganese oxide as a support material in PdNi. Here MN as a support material will supply the oxygen to the catalyst and Ni will adsorb the OH^- to oxidize the poisonous intermediates effectively. The possible reaction mechanism of electrooxidation of methanol at PdNi/MN is follows.

$$Pd + H_2O \rightarrow Pd(OH)_{ads} + H^+ + e^- \quad (1)$$

$$Pd + (CH_3OH) \rightarrow Pd(CH_3OH)_{ads} \quad (2)$$

$$Pd + (CH_3OH)_{ads} \rightarrow Pd(:COH) \quad (3)$$

$$Pd(:COH) + H_2O \rightarrow Pd(HCOOH)_{ads} + H^+ + e^- \quad (4)$$

$$Pd(HCOOH)_{ads} \rightarrow Pd(CO)_{ads} + H_2O \quad (5)$$

$$Pd(CO)_{ads} + Pd(OH)_{ads} \rightarrow 2Pd + CO_2 \uparrow + H_2O \quad (6)$$

$$Ni + H_2O \rightarrow Ni(OH)_{ads} + H^+ + e^- \quad (7)$$

$$Pd(CO)_{ads} + Ni(OH)_{ads} \rightarrow Pd + Ni + CO_2 \uparrow + H_2O \quad (8)$$

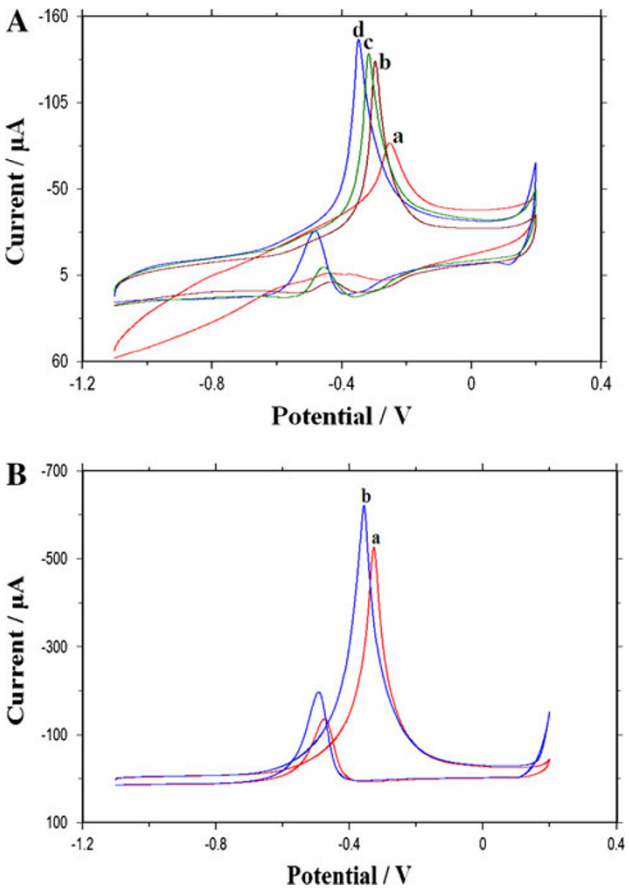

Fig. 5 **A** Cyclic voltammogrames of electrooxidation of Methanol at PdNi/MN in 1 M CH_3OH with *a* 1 M *b* 3 M *c* 6 M and *d* 9 M KOH; **B** *a* 6 M KOH/6 M CH_3OH and *b* 9 M KOH/6 M CH_3OH. (Scan rate 50 mV/s)

In general, $Pd(CO)_{ads}$ is treated as a poisonous intermediate which hinders the activity of Pd, Initially Pd will adsorb the OH^-, which further helps to degrade the poisonous intermediates (Reactions 1–6). In the presence of Ni as adatom to Pd, and being an oxophilic nature, it readily forms $Ni(OH)_{ads}$, which is supplied to the catalytic Pd, thereby the electrocatalytic activity was improved and the availability of active Pd sites were increased (Reactions 7, 8). Hence, the electrocatalytic activity of PdNi/MN was enhanced even in higher alkaline condition.

On increasing the Pd loading to 10 wt% on the MN material (Fig. 6Ab), the cyclic voltammogrames characteristics for 1 M KOH/1 M CH_3OH remained same as those obtained for the 5 wt% Pd/MN (Fig. 6Aa) nanocomposite material except that a higher current output has been obtained. Fig 6B shows the cyclic voltammogrames of PdNi/MN nanocomposite for 1 M KOH/1 M CH_3OH electrooxidation during the first 20 segments. The degree of reduction in current is lower as the number of segment increases from 1 to 20. The peak current remained almost constant. From these results, it is clear that the superior stability of the PdNi/MN electrode towards methanol electrooxidation over repetitive potential segment proves that the surface poisoning by the reaction intermediates does not affect the catalytic activity.

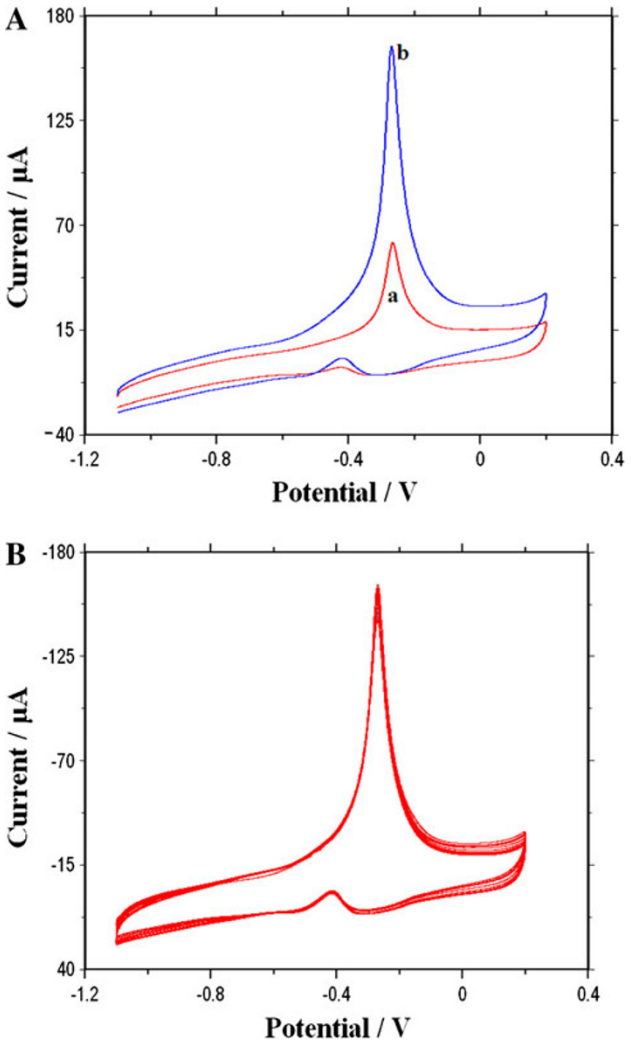

Fig. 6 **A** Cyclic voltammogrames of electrooxidation of 1 M KOH/1 M CH_3OH at *a* 5 wt% and *b* 10 wt% Pd in PdNi/MN; **B** CVs of 1 M KOH/1 M CH_3OH at PdNi/MN scanned for 20 segments (Scan rate 50 mV/s)

Conclusion

In the present work, nanocrystalline PdNi was coated on MN and was tested for its electrocatalytic oxidation of methanol. The experimental results show the prepared catalyst exhibits improved electrocatalytic activity towards methanol. The oxidation potential was shifted to a lower potential and the peak current was also increased. 5% and 10% Pd with Ni was tested for the electrooxidation of methanol. The relative backward oxidation current was shifted in the negative direction with increasing concentration. The maximum oxidation current was shown at 6 M KOH/9 M CH_3OH. The MN acts as a supportive material, which extracts the active oxygen from the electrolyte and oxidizes the intermediate.

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